INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS APPLIED TO THE CHEMICAL COMPOSITION OF STEEL

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ABSTRACT

In the technological application of steel, the knowledge of its chemical composition is of fundamental importance as it is directly related to various properties, such as, mechanical properties, corrosion resistance, temperability and others. Instrumental Neutron Activation Analysis, INAA, is an appropriate technique in the evaluation of the chemical composition of steel and other metallurgical materials due to the possibility of simultaneous determination of a great number of elements without the inconvenience of sample dissolution. Element determination is achieved with good accuracy and precision for major and minor constituents as well as for trace elements.

In this paper, INAA was used in the determination of As, Co, Cu, Mn, Mo, V and W in steel and iron samples and in certified reference materials. The obtained accuracy and precision were less than 10% for most of the elements confirming the possibility of its use in the study of metallic samples and in the certification of new reference materials.

I. INTRODUCTION

It is well known that the chemical composition of metallic materials plays an important role in the technological properties these materials present. Mechanical properties, corrosion resistance, temperability and other properties may be enhanced by the addition of suitable amounts of different elements to the materials. On the other hand, it is also important to control impurities from the manufacturing process which could influence negatively the characteristics of the material.

Many analytical techniques have been used in the chemical composition determination of metals and their alloys, such as atomic absorption spectroscopy, x-ray fluorescence spectroscopy, ICP spectroscopy, optical emission spectroscopy, ionic chromatography and activation analysis. Very few papers can be found in the literature dealing with the instrumental method of NAA applied to steel. It is possible to find radioactive sources other than nuclear reactors in the neutron production [1], absolute methods instead of the comparative one [2, 3] different particles in the activation process [4, 5, 6] and radiochemical separations [7, 8].

The purpose of this work is the optimization of the INAA technique to the determination of the chemical composition of metallic materials, specifically steel, in the Radiochemistry Supervision at IPEN. To attain this purpose, steel certified reference materials, CRM, were analyzed for validation of the method. Afterwards, the technique was applied in the analysis of steel and iron industrial samples.

II. EXPERIMENTAL

Sample Preparation. For the purpose of application of the comparative method of INAA, about 50 mg of sample filings were weighed in properly cleaned polyethylene vials and irradiated with elemental standards. The standards were prepared pipetting known element solutions into Whatmann filter paper which, after drying, were kept in polyethylene vials with the same geometry of the samples. Most of the samples were prepared in four replicates.

Irradiation. Two series of irradiation were used in this work, according to the half-life of the radioisotope being analyzed. The “short irradiation” was used for the determination of Mn and V. Sample aliquots and standards were irradiated for 30 s under a thermal neutron flux of 10^{12} n cm^{-2} s^{-1} at the pneumatic station of IEA-R1m Nuclear Reactor of IPEN. For the determination of the other elements “long irradiation” was used. Samples and standards were irradiated for 30 min in the irradiation facility of the reactor. The same aliquots used in the short irradiation were employed for this second irradiation.

TABLE 1. Radioisotopes used is this work

Irradiation	Energy, keV	Radioisotope	Half-life
Short -30 s	846,76	^{56}Mn	2,58 h
	1810,72	^{56}Mn	2,58 h
	1434,08	^{52}V	3,75 min
long - 30 min 1st measurement	72,00	^{187}W	23,9 h
	479,57	^{187}W	23,9 h
	140,22	^{99}Mo	65,9 h
	559,10	^{76}As	26,32 h
	1345,77	^{64}Cu	12,7 h
long - 30 min 2nd measurement	320,08	^{51}Cr	27,7 d
	810,77	^{58}Co	70,8 d
	1773,24	^{60}Co	5,3 y
	1332,50	^{60}Co	5,3 y

Table 1 summarizes the radioisotopes used, their gamma ray energies and half-lives. In the determination of Ni, the radioisotope ^{58}Co, formed in the ^{58}Ni (n,p)^{58}Co reaction was used [9].

Element determination. The induced gamma radiation of Mn and V were measured immediately after the irradiation. Samples were measured for 20 min and standards for 5 min. As, Cu, Mo and W were measured after a 2 day decay period. Co, Cr, and Ni were measured after an 1 month decay period. In both cases aliquots were measured for 1 h and standards for 30 min.

The measurement was performed using the following detector systems:

- GX 2020 CANBERRA HPGe detector, coupled to CANBERRA multi-channel system and eletronics;
- EGNC 25-190-R Eurysis HPGe detector coupled with Eurysis multi-channel system and eletronics.

Element concentration was calculated applying in-house softwares. For the short lived radionuclides, the radioactive decay was considered for the calculations.

III. RESULTS AND DISCUSSION

Table 2 presents the certified concentration values for the CRM, as supplied by the producers. For values not presented, there is no certified value available. Tables 3 and 4 show the results of INAA obtained in this work for CRM and for industrial samples of steel (S1 and S2) and iron (S3 and S4). One can notice that, even for the elements without certification or with informative values only, it was possible to obtain results. The uncertainty of the measurements is represented by the standard deviation for the sub-population of n aliquots of the samples or CRM.

Table 5 presents the number of aliquots analyzed as well as the relative standard deviation, σ_r (%) for the results in Tables 3 and 4, and the relative error, E_r (%) for results in Table 3.

Standard deviation is connected to the repeatability of the results and hence, to the precision of the method. The σ_r (%) values observed are less than 10% for the CRM, (except for Cu, V and W). This result is consistent with the precision expected for INAA. Relative error data are also less than 10% for the elements except for V, W, Mn and Cu in some of the CRM.

Although V and W present intense gamma ray peaks, the low concentration of these elements in the samples may cause this difficulty in the determination, with possible interference of the gamma rays of the other elements. Mn and V are measured as short lived radionuclides, and it implies in higher dead times for the detector, and so, precision is reduced.

TABLE 2. Certified values for the CRM used in this work[a]

CRM	**IPT 22**	**IPT 24**	**IPT 26**	**NBS 442**	**NBS 447**	**BCS 464**	**BCS 466/1**
Code	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Element	**Concentration (%)**						
As	-	-	-	-	-	0,0028±0,0005	0,017 ± 0,002
Co	-	0,045±0,004	-	0,13	-	0,054±0,001	-
Cr	16,21±0,03	17,81±0,05	13,69±0,04	16,1	23,72	25,75±0,07	17,65±0,04-
Cu	0,0500±0,0008	0,039±0,002	0,029±0,001	0,11	0,19	-	-
Mn	0,804±0,008	1,50±0,01	0,713±0,006	2,88	0,23	0,77±0,01	0,698 ± 0,008
Mo	-	2,54±0,03	0,070±0,04	0,12	0,059	-	2,19±0,01
Ni	0,143±0,007	9,93±0,05	0,413±0,004	9,9	13,26	20,70±0,05	8,61 ± 0,04
V	-	-	-	0,032	(0,03)	-	-
W	-	-	-	(0,08)	(0,06)	-	-

a. Information values in brackets

TABLE 3. Steel CRM element concentrations obtained in this work by INAA (10^{-3} %)[a]

	Certified Reference Material Concentration (10^{-3} %)						
Element	**1**	**2**	**3**	**4**	**5**	**6**	**7**
As	3,69±0,32	8,35±0,31	4,52±0,18	7,56±0,66	2,599±0,092	2,82±0,83	16,61±0,67
Co	26,7±1,4	41,8±1,7	24,98 ± 0,56	124,8±3,9	98,3±3,6	53,2±1,1	15,9±0,1
Cr[a]	15,44±0,60	17,64±0,76	13,62±0,73	15,34±0,94	22,77±0,94	25,08±1,25	16,11±0,35
Cu	48,5±2,7	34,5±3,1	17,9±3,1	102,2±9,5	198,27±0,22	27,65±0,92	20,3±2,5
Mn	767±28	1367±28	661,8±25,5	2584±87	220,9±6,3	785±17	669±11
Mo	7,5±1,9	2610±100	72,9±2,8	117,6±9,3	48,7±4,0	8,00±0,83	1975±45
Ni[a]	0,134±0,017	10,20±0,62	0,394±0,015	9,45±0,47	13,44±0,46	20,25±0,55	8,65±0,63
V	40,7±7,0	47,8±4,5	43,6±1,5	63,8±2,8	52,3±3,0	131,5±8,2	38,2±2,8
W	0,261±0,036	0,651±0,058	0,279±0,016	69,7±5,6	53,8±3,5	1,011±0,085	2,028±0,023

a. values in percentage

TABLE 4. Relative standard deviation and relative error (%) obtained in this work by INAA for steel CRM element concentration and metallic samples[a]

	Certified Reference Material							Metallic sample			
Element	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**S1**	**S2**	**S3**	**S4**
As	n = 4	4	4	4	4	4	4	4	4	4	4
	σ_r = 8,7	3,7	4,0	8,7	3,5	4,2	4,0	5,7	6,3	2,6	2,3
	E_r = -	-	-	-	-	6,0	2,3				
Co	8	8	8	8	6	8	2	8	8	8	8
	5,1	4,1	2,2	3,1	3,6	2,2	0,9	3,2	2,8	2,8	6,7
	-	7,1	-	4,0	-	1,5	-				
Cr	4	4	4	4	4	4	4	4	4	4	4
	3,9	4,3	5,4	5,7	4,1	5,0	2,2	3,4	2,7	9,8	4,7
	4,8	0,9	0,05	4,7	4,0	2,6	8,7				
Cu	4	2	4	3	3	2	4	4	3	4	4
	5,5	9,1	17,3	9,2	1,1	9,2	12,2	4,3	5,5	10,2	1,0
	3,0	11,5	3,8	7,1	4,4	-	-				
Mn	4	4	4	4	4	4	4	8	8	8	8
	3,6	2,0	8,6	3,4	2,9	2,2	1,7	7,5	1,8	1,2	4,9
	4,8	8,9	0,56	10,3	4,0	1,9	4,2				
Mo	4	4	4	4	4	4	4	4	4	4	4
	25,3	3,9	3,3	7,9	8,3	10,4	2,3	6,5	4,2	3,8	3,5
	-	2,8	0,03	2,0	17,4	-	9,8				
Ni	4	4	4	4	4	3	4	4	4	3	4
	12,5	6,1	3,9	5,0	3,4	2,7	7,3	4,5	3,4	13,0	23
	6,3	2,7	4,6	4,5	1,3	2,2	0,5				
V	4	4	4	4	4	4	4	4	3	1	4
	17,2	9,3	3,4	4,4	5,8	6,2	7,3	7,2	16,1	34	29
	-	-	-	99,4	74,3	-	-				
W	3	3	8	4	4	4	4	8	8	8	8
	13,8	15,3	5,7	8,0	6,5	8,4	1,1	5,4	5,4	12,2	5,3
	-	-	-	12,9	10,3	-	-				

a. n = number of aliquots analyzed - σ_r = relative standard deviation - E_r = relative error

TABLE 5. Element determination in metallic samples[a]

Element	Concentration (10^{-3} %)			
	S1	S2	S3	S4
As	3,15±0,18	3,82±0,24	2,382±0,062	3,110±0,071
Co	57,2±2,1	86,7±2,4	4,378±0,124	4,82±0,32
Cr[a]	11,76±0,41	18,21±0,49	0,143±0,014	0,1881±0,0089
Cu	109,7±4,7	154,9±8,5	27,5±2,8	236,1±2,3
Mn	700±52	877±16	1163±76	755±37
Mo	507±33	2076±88	52,1±2,0	52,1±1,8
Ni[a]	4,00±0,18	9,57±0,33	0,115±0,015	0,0212±0,0049
V	56,9±4,1	793±136	81±28	13,6±4,0
W	12,81±0,69	59,1±9,5	0,279±0,034	2,26±0,12

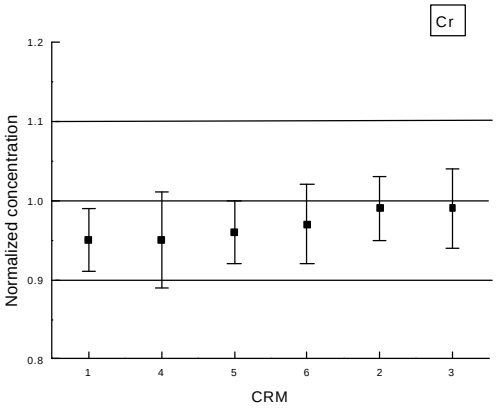
a. values in percentage

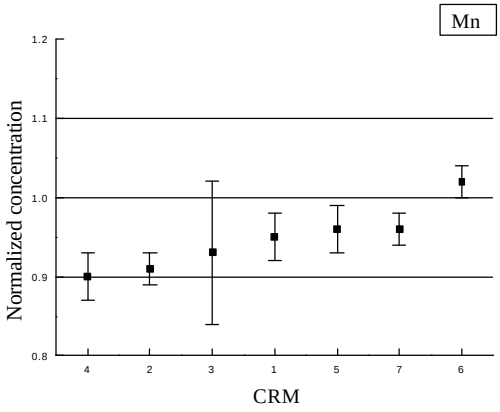
Figure 1 illustrates the data presented in Table 5 in terns of normalized concentration for some elements. Accuracy is inspected as the deviation from unit, while precision is represented by the dispersion of the values. It can be observed that most of the data are within the established limits of 10% for INAA (0,9 to 1,1). Figure 2 shows the z values for the CRM with uncertainties in the certified value. This parameter, used as an evaluation tool for quality systems, is given by the following expression [10]

$$z = \frac{C_a - C_r}{(\sigma_a^2 + \sigma_r^2)^{1/2}} \qquad (1)$$

where:
C_a is the concentration obtained in the lab. for the CRM;
C_r is the certified value or consensus value;
σ_a is the uncertainty in the analysis;
σ_r is the uncertainty in the certified value.

It is observed that most values are within the ±3 limit expected for INAA, confirming the suitability of the method.





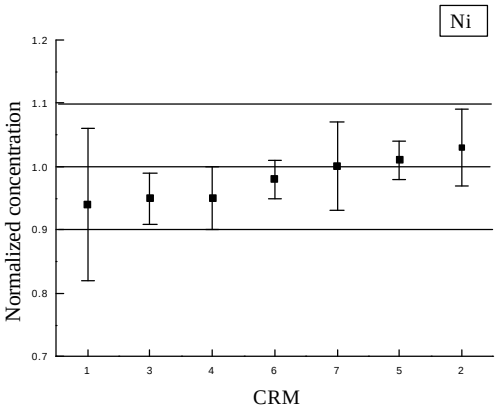
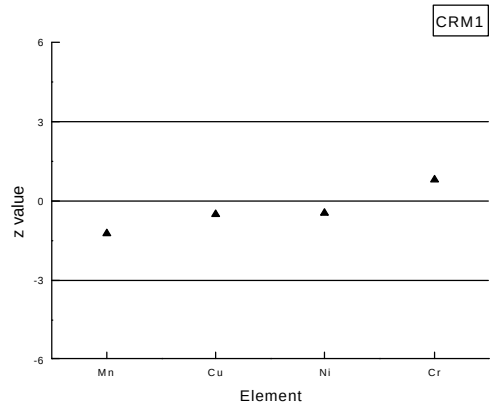
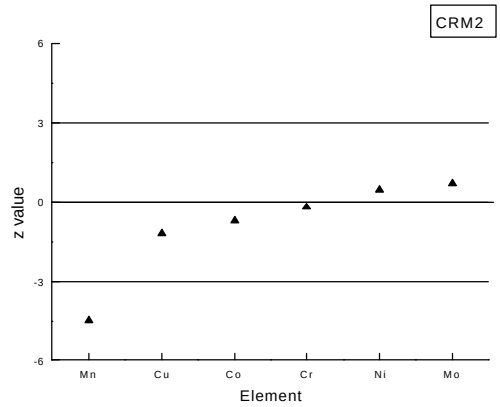
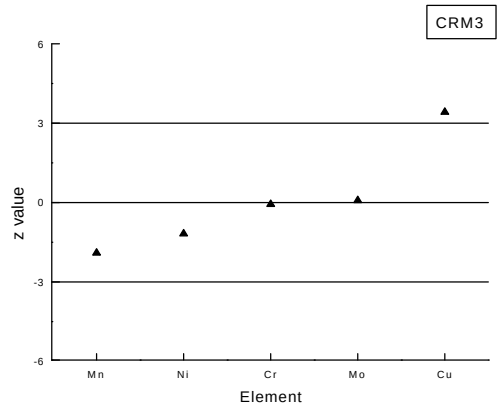
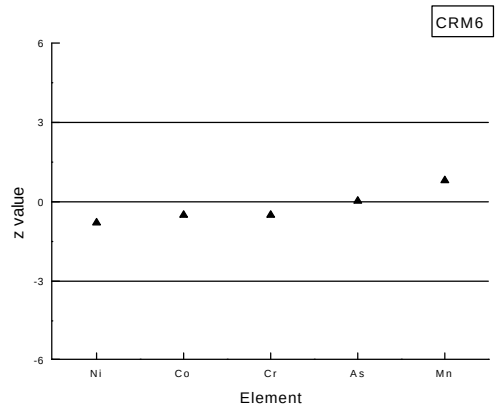


Figure 1. Normalized concentration for some elements, obtained in this work by INAA.









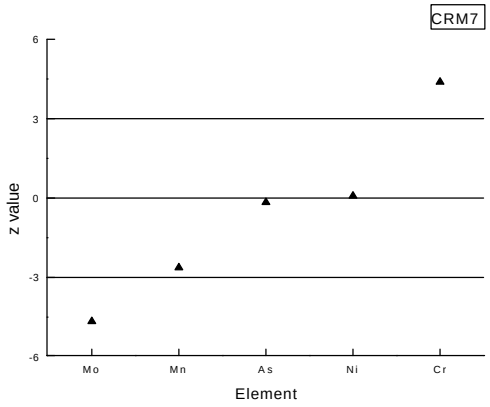


Figure 2. Z values obtained in this work for CRM1 to CRM7.

III. CONCLUSIONS

The results of this work show that the INAA technique may be used successfully in the determination of various elements in steel and iron samples, as well as in the certification of new CRM. For some elements as V and W it is still necessary further development of the method.

IV. REFERENCES

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